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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The mass change during electropolymerization and redox process was monitored for polypyrrole films using Quartz Crystal Microbalance Gravimetry. During reduction process the polypyrrole films which had incorporated large poly(4-styrene-sulfonate) anions showed a mass increase instead of decrease (cation doping). On the other hand, the polypyrrole film formed with a small ClO ₄ ⁻ anion showed a mass decrease (anion doping).			
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Quartz Crystal Microbalance Analysis: I. Evidence of Anion or Cation Insertion into Electropolymerized Conducting Polymers

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Introduction

Utilization of the quartz crystal microbalance (QCM) in conjunction with electrochemistry can allow one to determine the mass of polymer electrode and charge utilization simultaneously and in-situ under the conditions that the electrode is polarized electrochemically. This combination of measurements has already been used for the following cases; (i) electrodeposition of metals (1); (ii) dissolution of metals (Ni(2), Cu and Co(6)); (iii) redox process for conducting polymers (polypyrrole(3), polyaniline(4)) and a redox polymer (polyvinylferrocene)(5). The method is also advantageous for monitoring the mass change of conducting polymers like polypyrrole, polyaniline during electropolymerization and doping/undoping. The emphasis of this short note is to monitor polypyrrole growth on the electrode with time, and to survey ion motions into or out of the film during a subsequent reduction.

Polypyrrole films were formed with two different types of anions; one is small, the other is a large polymeric anion(7,8). In-situ monitoring of the mass change was made using QCM gravimetry for the above two cases, and the reduction processes at the two different films were observed. During the reduction process after polymer growth, the mass measurement of the polypyrrole films showed a decrease for polypyrrole films formed with ClO_4^- , which is consistent with anion undoping or movement out of the film. On the other hand, mass increased upon reduction of the film formed with poly(4-styrenesulfonate) anions, indicating that cations insert into the polymer film in order to maintain charge neutrality.



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Experimental

Shear mode 6MHz AT-cut quartz crystals obtained from Inficon (East Syracuse, NY) were used for this investigation. The crystals had vacuum deposited gold electrodes on both sides. The total projected area exposed to the solution was 0.33 cm^2 . The crystal oscillator circuit included a power source and an oscillator (Inficon XTC). The frequency was measured with a frequency counter (HP5384A) and measurements were sent to and stored in a personal computer (HP9816).

The experiments were carried out in a 4-necked glass cell. Two of the necks were used for the gas inlet and outlet, one for the reference electrode and the last one for the counter electrode (stainless steel /large surface area). The working electrode was the conducting polymer film deposited on the Au-coated quartz crystal in contact with the solution. The quartz plate was sealed to the cell with a silicone rubber sealant. The electrode potential was controlled by a potentiostat. The working electrode was grounded through the potentiostat. The reference electrodes employed in the present work were SCE(aqueous system) and Ag/AgNO₃(acetonitrile system).

Results and Discussion

Figure 1 shows mass change, charge, current variations of polypyrrole films during cyclic voltammetry. On the left side, polypyrrole was grown with a relatively smaller size anion (ClO_4^-), where the potential was scanned from 0.2V to 0.8V and reversed from 0.8V to -1.5V. At the potentials between 0.3 and 0.8V, the polymer grew at an almost constant rate. The polymer was then reduced between 0.3V and -1.5V, and the cathodic charge as well as mass change(decrease) were observed. As cathodic(negative) charge was consumed for the reduction of the film, at the same time anions were released from the film in order to maintain the charge neutrality.

On the contrary, the right figure shows a completely opposite behavior to the former one during the reduction process between -0.1 V and -1.3V. During reduction, this film which had incorporated the large poly(4-styrenesulfonate) anions showed a mass increase in stead of decrease. This suggests that the film incorporated cations(Na^+) during reduction to the neutral state. The net weight gain may also indicate some solvent incorporation(acetonitrile), but more

details of the process will be discussed in subsequent reports. The results support the fact found by T. Shimidzu et. al(7) and suggest that a conducting polymer film may be made either anion-inserting or cation-inserting by choice of the anion incorporated during electropolymerization. Small anions may move in or out during oxidation and reduction cycle, but large anions do not and cations must move out or in to maintain net charge neutrality during the cycles. Also, in the case of polypyrrole films formed with medium sized anions(e.g., tosylate, triflate, etc.), both anions and cations seem to move during redox process(9,10).

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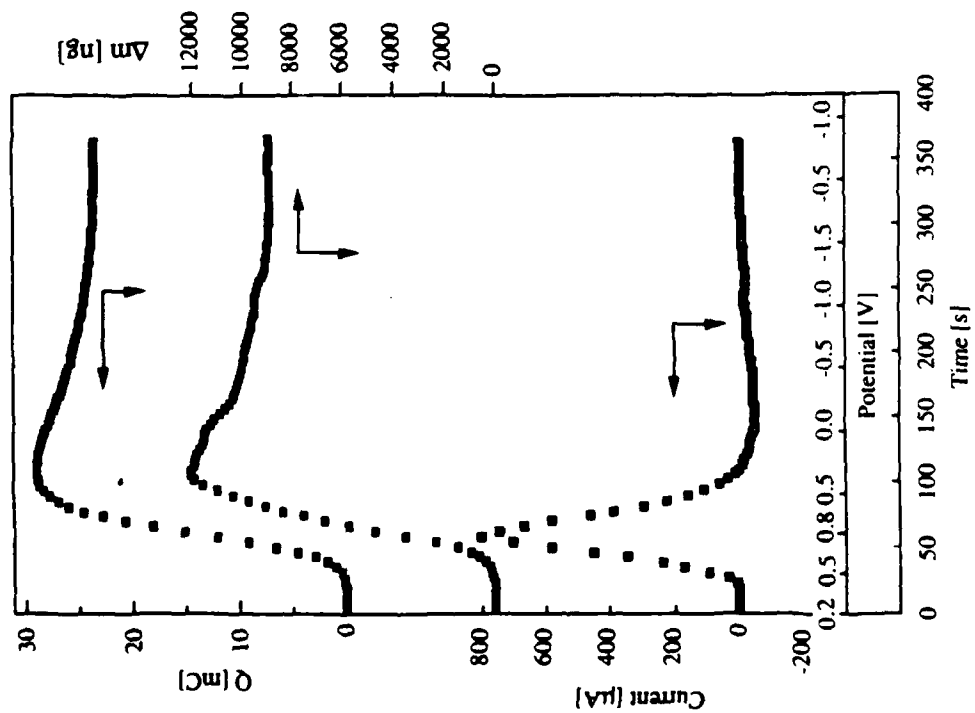
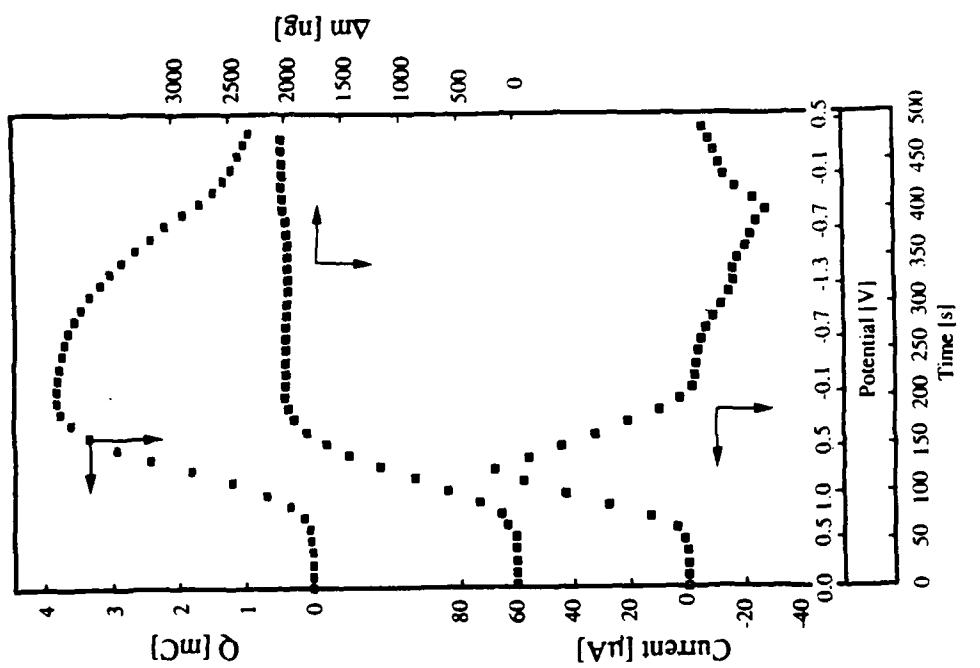


Figure caption

Fig.1 Mass change(Δm), charge(Q) and current variations as a function of time or potential during polypyrrole formation and reduction of films at a scan rate of 10 mV s^{-1} . Left: polypyrrole prepared prepared in 0.2 mol dm^{-3} pyrrole+ 0.2 mol dm^{-3} TBAClO_4 (aqueous); Right: polypyrrole prepared in (0.01 mol dm^{-3} pyrrole+ 0.01 mol dm^{-3} poly(sodium 4-styrenesulfonate))/acetonitrile.